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Europäisches Patentamt
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11 Publication number: **0 382 365 B1**

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EUROPEAN PATENT SPECIFICATION

- 45 Date of publication of patent specification: **21.06.95** 51 Int. Cl.⁶: **C08G 77/08, C08G 77/20, C08G 77/22, C08G 77/06**
- 21 Application number: **90300645.0**
- 22 Date of filing: **22.01.90**

54 Process for producing organosilicon products.

- 30 Priority: **09.02.89 GB 8902935**
- 43 Date of publication of application:
16.08.90 Bulletin 90/33
- 45 Publication of the grant of the patent:
21.06.95 Bulletin 95/25
- 84 Designated Contracting States:
BE CH DE ES FR GB IT LI NL
- 56 References cited:
- | | |
|------------------------|------------------------|
| EP-A- 0 039 299 | EP-A- 0 180 527 |
| EP-A- 0 264 336 | FR-A- 1 495 011 |
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Description

This invention relates to a process for the production of organosilicon products and is concerned in particular with a process for the condensation of organosilicon compounds having silicon-bonded hydroxyl groups.

In the synthesis of organosilicon products it is often desired to react organosilicon compounds containing silanol ($\equiv\text{SiOH}$) groups with other organosilicon compounds. Specific and commercially important examples of such a reaction occur in the production of triorganosiloxy end-stopped polydiorganosiloxanes and in the production of polysiloxanes having silicon-bonded organofunctional, for example mercaptoalkyl, groups. Triorganosiloxy end-stopped polydiorganosiloxanes and organofunctional polysiloxanes can be prepared by an equilibration process involving the reaction of silanol-terminated polydiorganosiloxanes with a source of end-stopping units or organofunctional siloxane units, such as hexamethyldisiloxane or cyclic organofunctional siloxanes, in the presence of an equilibration catalyst. Many such catalysts are known and include sulphuric acid, hydrochloric acid, Lewis acids, potassium hydroxide and tetramethylammonium hydroxide. Although effective in producing the desired polysiloxane such equilibration catalysts cause scission and random rearrangement of the siloxane bonds. As a result of such rearrangement the product often contains a significant proportion of low molecular weight siloxanes. For many applications, for example in the production of silicone elastomers the presence of such low molecular weight materials is undesirable. Random rearrangement of the siloxane bonds is also undesirable when the polysiloxane is to contain a planned arrangement of two or more types of organic substituents. In E.P. 0 039 229-A there is disclosed a process for the preparation of high molecular weight organopolysiloxanes by the catalysed polymerisation and rearrangement of lower molecular weight organopolysiloxanes, the process being characterised by the use of an alkaline catalyst and a tris(oxyalkyl)amine. The alkaline catalyst may be an alkaline metal or alkaline earth metal or their derivatives preferably Li, Na, K, Rb and Cs and their derivatives.

In U.S. Patent 3,642,693 there is disclosed a method for hydrolysing organic trialkoxysilane monomers such as methyltrialkoxysilane, phenyltrialkoxysilane or mixtures thereof using a Group II-A metal-containing hydrolysis catalyst such as barium hydroxide or calcium hydroxide.

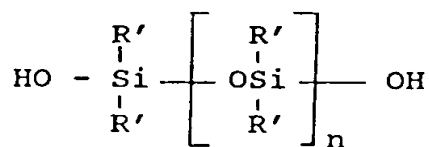
A method for the production of organosilicon products which avoids the occurrence of siloxane bond scission and rearrangement has been disclosed in British Patent 918 823. According to said method silanol-containing organosilicon compounds can be condensed with organosilicon compounds having $\equiv\text{SiOR}$ groups, wherein R is organic, employing catalysts which are certain salts of a phosphoric acid or a carboxylic acid with an amino compound. However, many such catalysts are liquids, or are not suitable for use at high temperatures or are not readily removable from the product. There has therefore existed a need for improved catalysts for the reaction of organosilicon compounds having $\equiv\text{SiOH}$ groups with those having $\equiv\text{SiOR}$ groups. In particular, the desired catalysts should be suitable for use in heterogeneous reaction systems thereby facilitating their separation from the desired reaction product and preferably enabling their recovery and re-use in batch processes or their application in a continuous process.

According to the present invention there is provided a process for the preparation of an organosilicon condensation product which comprises reacting together at a temperature of at least 50°C (A) at least one silanol-terminated polydiorganosiloxane having one or two silanol groups in the molecule and wherein the organic substituents are selected from monovalent hydrocarbon groups having from 1 to 18 carbon atoms and monovalent substituted hydrocarbon groups having from 1 to 10 carbon atoms said substituted hydrocarbon groups being non-acidic in character, and (B) an organosilicon compound having in the molecule at least one $-\text{OX}$ group wherein X represents an alkyl group having from 1 to 8 carbon atoms or an alkoxyalkyl group having from 2 to 8 carbon atoms, any remaining silicon-bonded substituents in the organosilicon compound being selected from monovalent hydrocarbon groups having from 1 to 18 carbon atoms and monovalent substituted hydrocarbon groups having from 1 to 10 carbon atoms, said substituted hydrocarbon groups being non-acidic in character, in the presence of a sole catalyst substance (C) which is strontium hydroxide and/or barium hydroxide and thereafter separating the organosilicon condensation product and the catalyst substance (C), or neutralising the catalyst substance (C).

The process of this invention may be applied in the production of condensation products of any types of substantially linear organosiloxane polymers (A) (which term includes oligomers) and organosilicon compounds (B) provided that (A) has therein bonded directly to a silicon atom at least one hydroxyl group and (B) at least one $-\text{OX}$ group similarly bonded. Thus the organosilicon compounds (B) may be organosilanes or organosiloxanes. As the silicon-bonded organic substituents in (A) and (B) there may be present monovalent hydrocarbon groups such as alkyl, alkenyl, aryl, aralkyl and alkaryl groups or non-acidic monovalent substituted hydrocarbon groups, that is groups not containing acidic substituents such as carboxyl, sulphate and sulphonic. Examples of operative non-acidic groups are amino-substituted alkyl and

aryl groups, mercaptoalkyl groups, haloalkyl groups, esterified carboxyalkyl groups and hydroxyalkyl groups. Specific examples of organic substituents which may be present in the reactants (A) and (B) employed in the process of this invention are methyl, ethyl, propyl, hexyl, dodecyl, tetradecyl, phenyl, xylyl, tolyl, phenylethyl, vinyl, allyl, hexenyl, $-R''NH_2$, $-R''NHCH_2CH_2NH_2$, $-R''SH$, $-R''Br$, $-R''Cl$ and $-R''OH$ wherein R'' represents a divalent organic group, preferably having less than 8 carbon atoms, for example alkylene, e.g. $-(CH_2)_3-$, $-(CH_2)_4-$ and $-CH_2CHCH_3CH_2-$, arylene e.g. $-C_6H_4-$ and alkarylene e.g. $-(C_6H_5CH_2)-$.

Although applicable in the production of a variety of organosilicon products by a condensation reaction the process of this invention is of particular interest with regard to the manufacture of end-stopped polydiorganosiloxanes and polyorganosiloxanes having therein organofunctional substituents, that is substituted hydrocarbon groups such as amidoalkyl, chloroalkyl, mercaptoalkyl, cyanoalkyl and hydroxyalkyl groups. Preferably, therefore, organosiloxane polymers (A) are silanol-terminated polydiorganosiloxanes, that is substantially linear organosiloxane polymers or oligomers having a hydroxyl group attached to each terminal silicon atom and organosilicon compounds (B) are silanes having from 1 to 3 $-OX$ groups per molecule. The preferred organosiloxane polymers (A) can be represented by the average general formula



wherein each R' represents an organic substituent as hereinabove defined and n is an integer having a value of from 1 to about 300. In commercial practice of the invention at least 50% of the total R' substituents will normally be methyl with any remaining substituents being selected from vinyl, phenyl and haloalkyl. Said hydroxyl-terminated polydiorganosiloxanes are well known, commercially available materials and can be prepared by known methods. The low molecular weight polymers and oligomers can be obtained by the hydrolysis of diorganodihalosilanes. These may then be subjected to polymerisation procedures as desired employing equilibration or condensation catalysts to obtain polydiorganosiloxanes of the desired molecular weight. The preferred organosilicon compounds (B) may be represented by the general formula $GySi(OX)_{4-y}$ wherein y has a value of 1, 2 or 3, G represents a monovalent hydrocarbon group having from 1 to 18 carbon atoms or a monovalent substituted hydrocarbon group having from 1 to 10 carbon atoms and X is as hereinbefore defined. Preferably X represents an alkyl group having from 1 to 3 inclusive carbon atoms and each G is selected from methyl, phenyl, vinyl, aminoalkyl, (polyamino)alkyl, mercaptoalkyl, amidoalkyl and cyanoalkyl. Specific examples of the preferred organosilicon compounds (B) are, therefore, $(CH_3)_3Si(OC_2H_5)$, $C_6H_5Si(OCH_3)_3$, $(CH_2=CH)(CH_3)(C_6H_5)SiOCH_3$, $CH_3(CH_2=CH)Si(OC_2H_5)_2$, $H_2N(CH_2)_3Si(CH_3)(OC_4H_9)_2$, $H_2NCH_2CH_2NHCH_2CH_2CH_3CH_2Si(CH_3)(OC_2H_5)_2$, $H_2NCH_2CH_2NH(CH_2)_3Si(OC_2H_5)_3$, $HS(CH_2)_3SiCH_3(OC_3H_7)_2$, $Cl(CH_2)_3Si(OCH_3)_3$ and $F_3C(CH_2)_4Si(CH_3)(OC_2H_5)_2$.

As the catalyst substance (C) there is employed strontium hydroxide or barium hydroxide or both. They may be employed in their anhydrous or in their hydrated forms. The particle size of the catalyst substance (C) is not critical. Generally, the smaller the particles the greater is the catalytic surface available for a given weight of catalyst. However, very fine particle size powders may be more difficult to remove from the condensation product.

The process of this invention involves reacting together organosiloxane (A) and organosilicon compound (B) in the presence of catalyst (C) at a temperature of at least $50^\circ C$. Reaction temperatures from $50^\circ C$ to about $250^\circ C$ may be employed. Reaction at the lower temperatures is, however, slow and the use of the higher temperatures is generally economically undesirable in terms of energy costs or where one or both reactants are volatile. In general therefore we prefer to carry out the reaction between (A) and (B) at a temperature in the range from about $60^\circ C$ to about $180^\circ C$. Volatile by-products and excess volatile reactant may be removed by distillation, if necessary or desired under reduced pressure, or by any other suitable means.

One method of carrying out the process of this invention is by way of a batch procedure. For example, the catalyst may be dispersed in the mixture of (A) and (B) and the mixture raised to the required reaction temperature. Alternatively, the catalyst may be dispersed in either (A) or (B) prior to bringing all of the reaction components together and raising the temperature. Advantageously the mixture is agitated during the reaction period to maintain the catalyst in suspension. Sufficient catalyst is employed to achieve the desired rate of condensation having regard to the nature and geometry of the processing equipment, temperature and other factors. From considerations of speed of reaction and economy of operation we prefer to employ from about 0.001 to about 5% by weight of the catalyst based on the total weight of the

reactants (A) and (B). Termination of the condensation reaction, may be achieved by lowering the temperature of the mixture and/or by separation of the catalyst, for example by filtration, or neutralisation.

Because of their heterogeneous nature the catalysts (C) are particularly adapted for use in processes involving manufacture on a continuous, rather than a batch, basis. Properly employed such so-called 'continuous processes' avoid the delays and costs common to batch processing, for example those involved in the charging and discharging of the reaction vessel and separation of the catalyst material from its admixture with the product. Thus, for example, the process of this invention may be advantageously employed for the continuous production of end-stopped and/or organofunctional siloxane polymers. When carrying out the process of this invention in a continuous mode contact between the catalyst material and the reactants (A) and (B) may be achieved by passing the mixture of (A) and (B) over or through a bed containing the catalyst material (C). When employing viscous reactants or products it may be necessary to adjust the porosity of the bed by granulation of the catalyst or other means. We have found that a particularly suitable form of bed for continuous operation can be obtained by depositing the catalyst substance in or on a particulate material, for example silica, having a particle size appropriate to the desired porosity of the bed

If desired the condensation product obtained by the reaction of (A) and (B) can be subjected to a polymerisation step which comprises contacting it with a second catalyst which is effective in catalysing the condensation of residual silanol groups in the condensation product with each other. Preferred as catalysts for this purpose are the borates and phosphates of sodium and potassium, for example Na_3PO_4 and $\text{K}_2\text{B}_4\text{O}_7$. Such polymerisation may be performed as a separate polymerisation procedure following recovery of the condensation product from the reaction mixture. More conveniently, however, when batch processing is employed, the second (polymerisation) catalyst may be added to the reaction mixture prior to separation and recovery of the condensation product.

The condensation products obtained by the process of this invention may be employed in any of the variety of applications known for the corresponding products produced by prior art processes. For example, they may be used as textile treatments to impart water repellency and/or softness, as components of paper coating compositions, as heat transfer fluids and in the production of adhesives and sealing materials.

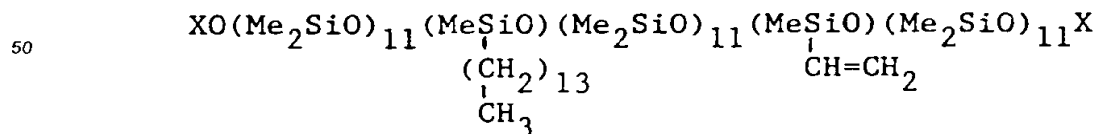
The following Examples in which Me represents the methyl group and Vi the vinyl group illustrate the invention.

Example 1

201g of a silanol-terminated polydimethylsiloxane, having a silicon-bonded OH content of 12,408 ppm, viscosity of $87.2 \times 10^{-6} \text{ m}^2/\text{s}$ at 25°C and Mn of 2740, was mixed with 18.4g of $\text{ViMe}_2\text{Si}(\text{OMe})$ and 2.03g of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. The mixture was agitated vigorously and heated to reflux temperature (88°C) at atmospheric pressure for 4 hours. The temperature of the reaction mixture was then raised to 130°C for a further 4 hour period, after which the mixture was allowed to cool and filtered to remove the catalyst. A vinyl dimethylsilyl-terminated polydimethylsiloxane was obtained having a residual silicon-bonded hydroxyl content of 417 ppm, a viscosity at 25°C of $128 \times 10^{-6} \text{ m}^2/\text{s}$ and a vinyl content of 1.81 by weight (theory = 1.95%).

Example 2

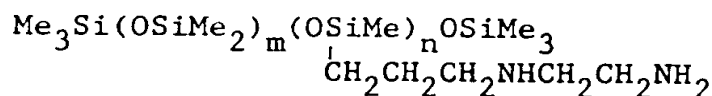
To $\text{HO}(\text{Me}_2\text{SiO})_{11}\text{H}$ (1053g) were added with mixing $(\text{MeO})_2\text{MeSi}(\text{CH}_2)_{13}\text{CH}_3$ (124g), $(\text{MeO})_2\text{MeSiCH}=\text{CH}_2$ (54g) and strontium hydroxide (12.31g). The mixture was then heated under reflux at 120°C for 4 hours, allowed to cool and filtered to remove the strontium hydroxide. The product was heated to 120°C under a pressure of 5 mbar to remove volatile substances and leave a polymer having the average formula



in which about 50% of the X groups are Me groups and the remainder H atoms.

Example 3

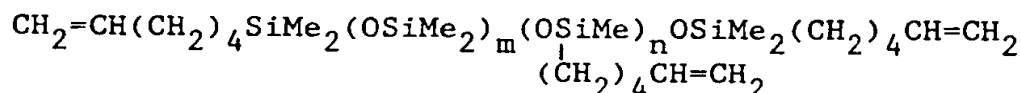
200g of an α,ω silanol-terminated polydimethylsiloxane of Mn 3300 and viscosity of 92×10^{-6} m²/s at 25°C, was mixed with 12.5g of (MeO)₂SiMeCH₂CH₂CH₂NHCH₂CH₂NH₂ and 5.92g of Me₃SiOMe. Barium hydroxide octahydrate, 0.2g was added to the mixture which was then refluxed at 85°C for four hours at atmospheric pressure. Trisodium orthophosphate dodecahydrate, 0.2g was added to the mixture which was then heated to 104°C at -0.99 bar gauge pressure for 4 hours. During this time volatiles were removed by distillation. The reaction mixture was then cooled and filtered to yield 190g of an aminosiloxane polymer of average structure



where m/n = 48/1 and having a viscosity of 211×10^{-6} m²/s at 25°C and a non-volatile content of 95.5% wt/wt measured over 2 hours at 150°C.

Example 4

800g of an α,ω silanol-terminated siloxane of average structure HO(SiMe₂O)_nH where n = about 35, was mixed together with 16.6g of CH₂=CHCH₂CH₂CH₂CH₂SiMe₂OMe and 41.5g of CH₂=CHCH₂CH₂CH₂CH₂SiMe(OMe)₂. Ba(OH)₂·8H₂O, 0.86g was added to the mixture which was then refluxed for six hours at 90°C and atmospheric pressure. After this time Na₃PO₄·12H₂O, 0.45g was added to the mixture and heating was continued at 105°C and 5-10 mm.Hg pressure for a further 3 hours. During this time methanol and water were removed by distillation. The mixture was cooled and filtered to yield 795g of a siloxane polymer of average structure



where m/n = 48.5/1 and having a viscosity of 185×10^{-6} m²/s at 25°C and a residual hydroxyl content of 150 ppm by weight (as OH).

Example 5

300g of an α,ω silanol-terminated siloxane of average structure HO(SiMe₂O)_nH, where n = 11, was mixed with 6g of Me₃SiOMe and 10g of cumene-an internal standard. Sr(OH)₂·8H₂O (7.4g) was added to the mixture at 120°C. Heating was continued at 110°C for an hour at atmospheric pressure during which time samples were taken periodically via a septum and analysed by capillary gas liquid chromatography. Reaction of HO(SiMe₂O)₁₁H and Me₃SiOMe was observed with the liberation of MeOH and the formation of Me₃SiOSi- bond.

The weight and hence molar concentration of Me₃SiOMe was calculated for each sample. Analysis of the data indicates a pseudo first-order reaction. Integrated rate expressions were plotted versus time, from which a rate constant of 6.67×10^{-4} per second at 110°C was calculated for the reaction of Me₃SiOMe and HOSi=.

Claims

1. A process for the preparation of an organosilicon condensation product which comprises reacting together at a temperature of at least 50°C (A) at least one silanol-terminated polydiorganosiloxane having one or two silanol groups in the molecule and wherein the organic substituents are selected from monovalent hydrocarbon groups having from 1 to 18 carbon atoms and monovalent substituted hydrocarbon groups having from 1 to 10 carbon atoms said substituted hydrocarbon groups being non-acidic in character, and (B) an organosilicon compound having in the molecule at least one -OX group wherein X represents an alkyl group having from 1 to 8 carbon atoms or an alkoxyalkyl group having

- from 2 to 8 carbon atoms, any remaining silicon-bonded substituents in the organosilicon compound being selected from monovalent hydrocarbon groups having from 1 to 18 carbon atoms and monovalent substituted hydrocarbon groups having from 1 to 10 carbon atoms, said substituted hydrocarbon groups being non-acidic in character, in the presence of a sole catalyst substance (C) which is strontium hydroxide and/or barium hydroxide and thereafter separating the organosilicon condensation product and the catalyst substance (C), or neutralising the catalyst substance (C).
2. A process as claimed in Claim 1 wherein (A) and (B) are reacted at a temperature in the range from 60 °C to 180 °C.
 3. A process as claimed in Claim 1 or Claim 2 wherein organosiloxane polymer (A) is a silanol-terminated polydiorganosiloxane.
 4. A process as claimed in any one of the preceding claims wherein (B) is a compound falling within the general formula $G_ySi(OX)_{4-y}$ wherein y has a value of 1, 2 or 3, G represents a monovalent hydrocarbon group having from 1 to 18 carbon atoms or a monovalent substituted hydrocarbon group having from 1 to 10 carbon atoms and X represents an alkyl group having from 1 to 8 carbon atoms or an alkoxyalkyl group having from 2 to 8 carbon atoms.
 5. A process as claimed in any one of the preceding claims wherein X represents an alkyl group having from 1 to 3 carbon atoms.
 6. A process as claimed in any one of the preceding claims which comprises passing a mixture of (A) and (B) over or through a bed containing (C).
 7. A process as claimed in any one of the preceding claims wherein (C) is present dispersed in or on a particulate silica.
 8. A process as claimed in any one of the preceding claims which also comprises contacting the condensation product with a second catalyst which is effective in catalysing the reaction of at least some of the residual silanol groups in said product with each other.

Patentansprüche

1. Verfahren zur Herstellung eines Organosiliciumkondensationsproduktes, das umfaßt, daß man bei einer Temperatur von mindestens 50 °C (A) mindestens ein Polydiorganosiloxan mit Silanolendgruppen mit ein oder zwei Silanolgruppen im Molekül, wobei die organischen Substituenten ausgewählt sind aus monovalenten Kohlenwasserstoffgruppen mit 1 bis 18 Kohlenstoffatomen und monovalenten substituierten Kohlenwasserstoffgruppen mit 1 bis 10 Kohlenstoffatomen, wobei die substituierten Kohlenwasserstoffgruppen nicht sauer sind, mit (B) einer Organosiliciumverbindung mit mindestens einer -OX-Gruppe im Molekül, worin X eine Alkylgruppe mit 1 bis 8 Kohlenstoffatomen oder eine Alkoxyalkylgruppe mit 2 bis 8 Kohlenstoffatomen bedeutet, wobei alle verbleibenden siliciumgebundenen Substituenten in der Organosiliciumverbindung ausgewählt sind aus monovalenten Kohlenwasserstoffgruppen mit 1 bis 18 Kohlenstoffatomen und monovalenten substituierten Kohlenwasserstoffgruppen mit 1 bis 10 Kohlenstoffatomen, wobei die substituierten Kohlenwasserstoffgruppen nicht sauer sind, in Gegenwart einer einzigen Katalysatorsubstanz (C), die Strontiumhydroxid und/oder Bariumhydroxid ist, umsetzt und danach das Organosiliciumkondensationsprodukt und die Katalysatorsubstanz (C) trennt oder die Katalysatorsubstanz (C) neutralisiert.
2. Verfahren nach Anspruch 1, worin (A) und (B) bei einer Temperatur im Bereich von 60 °C bis 180 °C miteinander umgesetzt werden.
3. Verfahren nach Anspruch 1 oder Anspruch 2, worin das Organosiloxanpolymer (A) ein Polydiorganosiloxan mit Silanolendgruppen ist.
4. Verfahren nach einem der vorhergehenden Ansprüche, worin (B) eine Verbindung ist, die unter die allgemeine Formel $G_ySi(OX)_{4-y}$ fällt, worin y einen Wert von 1, 2 oder 3 hat, G eine monovalente Kohlenwasserstoffgruppe mit 1 bis 18 Kohlenstoffatomen oder eine monovalente substituierte Kohlen-

wasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen bedeutet und X eine Alkylgruppe mit 1 bis 8 Kohlenstoffatomen oder eine Alkoxyalkylgruppe mit 2 bis 8 Kohlenstoffatomen bedeutet.

- 5 5. Verfahren nach einem der vorhergehenden Ansprüche, worin X eine Alkylgruppe mit 1 bis 3 Kohlenstoffatomen bedeutet.
6. Verfahren nach einem der vorhergehenden Ansprüche, umfassend, daß man eine Mischung von (A) und (B) über oder durch ein Bett, das (C) enthält, leitet.
- 10 7. Verfahren nach einem der vorhergehenden Ansprüche, worin (C) dispergiert in oder auf einem teilchenförmigen Siliciumdioxid vorhanden ist.
8. Verfahren nach einem der vorhergehenden Ansprüche, umfassend, daß man das Kondensationsprodukt mit einem zweiten Katalysator in Kontakt bringt, der die Reaktion mindestens einiger restlicher Silanolgruppen in dem Produkt miteinander katalysieren kann.

Revendications

- 20 1. Procédé pour la préparation d'un produit de condensation organosilicié, qui comprend la réaction, à une température d'au moins 50 °C, de (A) au moins un polydiorganosiloxane à terminaisons silanols ayant un ou deux groupes silanols dans la molécule et dans lequel les substituants organiques sont choisis parmi les groupes hydrocarbonés monovalents ayant de 1 à 18 atomes de carbone et les groupes hydrocarbonés monovalents substitués ayant de 1 à 10 atomes de carbone, lesdits groupes hydrocarbonés substitués étant de caractère non acide, et de (B) un composé organosilicié ayant dans la molécule au moins un groupe -OX dans lequel X représente un groupe alkyle ayant de 1 à 8 atomes de carbone ou un groupe alkoxyalkyle ayant de 2 à 8 atomes de carbone, les éventuels substituants liés au silicium restant dans le composé organosilicié étant choisis parmi les groupes hydrocarbonés monovalents ayant de 1 à 18 atomes de carbone et les groupes hydrocarbonés monovalents substitués ayant de 1 à 10 atomes de carbone, lesdits groupes hydrocarbonés substitués étant de caractère non acide, en présence d'une seule substance catalytique (C) qui est l'hydroxyde de strontium et/ou l'hydroxyde de baryum, puis la séparation du produit de condensation organosilicié et de la substance catalytique (C), ou la neutralisation de la substance catalytique (C).
- 35 2. Procédé selon la revendication 1, dans lequel on fait réagir (A) et (B) à une température dans la gamme de 60 °C à 180 °C.
3. Procédé selon la revendication 1 ou la revendication 2, dans lequel le polymère d'organosiloxane (A) est un polydiorganosiloxane à terminaisons silanols.
- 40 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel (B) est un composé ayant la formule générale $GySi(OX)_{4-y}$ où y est 1, 2 ou 3, G représente un groupe hydrocarboné monovalent ayant de 1 à 18 atomes de carbone ou un groupe hydrocarboné monovalent substitué ayant de 1 à 10 atomes de carbone et X représente un groupe alkyle ayant de 1 à 8 atomes de carbone ou un groupe alkoxyalkyle ayant de 2 à 8 atomes de carbone.
- 45 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel X représente un groupe alkyle ayant de 1 à 3 atomes de carbone.
- 50 6. Procédé selon l'une quelconque des revendications précédentes, qui comprend le passage d'un mélange de (A) et de (B) sur ou au travers d'un lit contenant (C).
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel (C) est présent, dispersé dans ou sur une silice particulière.
- 55 8. Procédé selon l'une quelconque des revendications précédentes, qui comprend aussi la mise en contact du produit de condensation avec un second catalyseur qui est efficace pour catalyser la réaction d'au moins certains des groupes silanols résiduels dans ledit produit entre eux.

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